Description

[0003] The present invention relates to novel methods to produce photonic crystals on substrate, and more particularly, to a method for synthesizing an inverted titania [[opals]] photonic crystal on substrate.

[0005] Photonic crystals have become one of the most interesting research areas in chemistry and material science engineering for their applications in chemical separation, catalysis, sorption, chromatography, optical sensors, optical ~~waveguids~~ waveguides, lasers, future optical circuits, photovoltaic cells (conventional p-n junction solar cells and [[die]] dye-sensitized titania solar cells), and battery materials. Three-dimensionally ordered ~~macroporous~~ inverted titania photonic crystals in particular has applications in chemical separation, catalysis, full band gap devices, photonic materials, and solar cells.

[0006] Colloidal photonic crystals are materials that have a periodic modulation of low and high refractive index regions with a lattice constant comparable to the wavelength of light. Inverse opals are photonic crystals that have a regular repetition of air which has a lower refractive index of 1 and high refractive index material such as titania which has a refractive index of 2.8 for rutile. ~~Photonic crystals have the property of filtering white light that is depending on their lattice constant they can forbid the propagation of a particular range of wavelengths from propagation through the material, which is reflected instead, and we have a pseudo band gap there. And the remaining wavelengths can pass through the crystal.~~ In order to have a complete band gap refractive index of the wall should be higher than 2.8. And inverted titania ~~inverse opals~~ photonic

crystals fit this description closely. The fabrication of photonic crystals are relatively simple, rapid, and economic.

[0007] Some of the applications of the photonic crystals are in optical sensors, optical circuits and waveguides, Laser, Photovoltaic cells (conventional p-n junction solar cells and [[die]] dye-sensitized titania solar cells), catalysis, sorption, chromatography, and battery materials.

[0008] Many papers and patents have been written on making ordered ~~macroporous~~ inverted titania [[opals]] photonic crystals in powder format but only a handful of scientific papers introduced methods to make such structures on substrate such as glass, ~~fluoride~~ fluorine doped tin oxide (FTO) coated glass, [[and]] or indium-doped tin oxide (ITO) coated glass.

[0009] For example, a method to make ~~macroporous~~ inverted titania [[opals]] photonic crystal powder was introduced by Richel and Johnson (Applied Physics Letters, 2000, 76, No. 14, 1816-1818). In this method a polystyrene colloidal crystal powder was assembled on a filter paper. The building blocks of this [[power]] powder are polystyrene spheres of size 400 nm. Then the polystyrene colloidal powder was removed from the filter paper and moved to a nitrogen glove box where it is infiltrated by an alkoxide precursor using a vacuum set up. When the alkoxide precursor soaked completely into the voids of the polystyrene template, the powder is removed from the glove box and let the alkoxide to hydrolyze slowly with the moisture in the air for a few hours. Then ~~to calcine the alkoxide inside the powder and to remove the polystyrene template it~~ the powder is placed in a tube furnace under air flow and heat it 575.degree. C. and stayed at

575.degree. C. for 8 hours. The end-material is an ~~inverse~~ inverted titania [[opals]] photonic crystal powder.

[0010] First of all, the optical quality of the ~~macroporous~~ inverted titania photonic crystal powder of the last example is not as good as it should be for industry applications. Secondly, the possible applications for these materials are limited because they are not produced on a conductive substrate. Thirdly, the glove box used here is very expensive and adds to the complexity of the process.

[0011] One of a very few methods introduced to date on making ~~macroporous~~ inverted titania [[opals]] photonic crystal film on substrate was set forth by Kuai and Badilescu (Advanced Materials, 15, No. 1, 2000). In this method silica spheres of the size 309 nm was used to make a silica template on substrate using convective assembly process. Then the film was heated at 600.degree. C. for 1 hour to make necking between silica spheres to increase the film's mechanical stability and to facilitate the template's removal later in the process.

[0012] Here they used sol-gel method to infiltrate a silica template. The solution prepared by mixing Titanium tetraisopropoxide (TTIP), Anhydrous ethanol, diethanolamine (DEA), and deionized water with molar ratio of 1:40:0.6:3.3. Silica template was immersed into the sol solution for 5 minutes to infiltrate the sol into voids of the template by a capillary force. Then the template was pulled out of the solution at a rate of 2.5 mm/s with a [[deep]] dip-coating equipment and let it hydrolyze slowly with the air moisture. The authors pointed out that the immersion and the withdrawing speed is very critical to making a good ~~inverse~~ inverted titania

[[opals]] photonic crystal film. At this stage of process the amorphous titania inside the template voids was densified and crystallized at 520.degree. C. in a tube furnace under air flow. ~~The infiltration and densification steps were repeated for 10 times to fill most of the voids inside the silica The titania-silica composite film on substrate produced in the preceding steps was immersed in a warm template.~~

[0013] The infiltration and densification steps were repeated for 10 times to fill most of the voids inside the silica. The titania-silica composite film on substrate produced in the preceding steps was immersed in a warm (60.degree. C.) aqueous NaOH solution (20%) for 24 hours to remove silica template. The result was an ~~inverse~~ inverted titania [[opals]] photonic crystal film on glass microslide.

[0014] The ~~macroporous~~ inverted titania photonic crystal film made by Kuai and Badilescu shows a good quality optical properties (transmission [[deep]] dip in its UV-VIS transmission characteristic) and the SEM characteristic of the film shows a long-range order. Of course, the transmission [[deep]] dip here is not sharp which limits its practical photonics application.

[0015] One of the main drawbacks of the preceding method to make ~~a inverse titania opal~~ an inverted titania photonic crystal film on glass substrate, as it was mentioned in the paper, was that NaOH solution would weaken the adhesion of the film to the glass substrate which causes the film to be separated from the substrate.

[0016] Also, in the preceding method a precise [[deep]] dip-coating immersion and withdraw

rate is crucial to the quality of the ~~inverse~~ inverted titania photonic crystal film. In addition, too many steps are involved in making ~~a macroporous~~ an inverted titania photonic crystal film on a substrate in this method. These would contribute to the overall high cost of the production.

[0018] Negatively charged polystyrene particles were stabilized by using surfactant sodium dodecyl sulfate (SDS). This increases the mechanical stability of the future template by producing necking between the particles. The increased necking between the particles keep the structure stable during infiltration, and also during the ~~calcinations~~ calcination. These particles were used to make polystyrene opals film on a glass, Indium Tin Oxide (ITO), [[or]] Fluorine doped Tin Oxide (FTO), silicon wafer, quartz, or mica substrate.

[0019] A centrifuge ~~(Falcon tube)~~ tube was half-filled with a diluted titanium precursor such as titanium(iv) isopropoxide (TiPT), titanium(iv) ethoxide (TEOT), titanium(iv) butoxide, titanium(iv) tert-butoxide, titanium(iv) methoxide, or titanium(iv) propoxide with anhydrous ethanol. Then the polystyrene template on a substrate was dropped into the ~~Falcon~~ centrifuge tube vertically. The degree of dilution is crucial to keep the structure of the template intact. After trying different dilution percentages it was obvious that dilution factors of less than 4 V % had little destructive effect on the polystyrene templates.

[0020] The centrifuge speed dial was set at 1200 rpm to 3600 rpm. ~~depending on the size of the centrifuge equipment. Basically, the smaller the machine is the faster it should turn to produce same gravitational effect.~~ And it was kept turning for 30 to 60 minutes.

[0021] After each centrifuge step was done, the film was taken out of the tube and placed in a loosely closed container. The infiltrated template was stored in the container for at least 6 hours. This resting period is necessary to let the precursor to hydrolyze and form an amorphous titania inside the voids of the polystyrene template. Then the template is put inside the ~~Falcon~~ centrifuge tube and it is gone through another centrifuge step.

[0022] Based on my results the number of the centrifuge step repetitions was at least 5 times to produce a stable and well ordered ~~inverse~~ inverted titania photonic crystal film on a substrate when a dilution factor of 4 V % of precursor was used. Of course, one could repeat the infiltration step until almost all the voids inside the template were filled with the titania. This could be figured out by following UV-VIS characteristics in particular the wavelength of the stop [[band]] gap on the ~~absorption~~ UV-Vis spectrum as it moved to higher wavelengths (red-shift) with each infiltration step. This is found from the light absorption against wavelength plot produced by a UV-VIS spectrophotometer. When this peak does not move to higher bandwidths anymore it mean all voids inside the template is almost filled.

[0023] The UV-VIS characterization of the films indicated the following. The higher the concentrations of the solutions were the faster the degradation of the films ~~(smaller stop band gap peak)~~. At the same time the more concentrated the solution was the higher the red-shift jump resulted for the film. So to optimize the infiltration the concentration should be very low. As mentioned above concentrations of 4 V % (4 volume percent) and lower gave very good results.

[0029] d) Temperature remained at 450.degree. C. for 3 hours; and

[0031] This heating procedure is needed for two reasons, first to remove the [[latex]] polystyrene through gasifying and burning ~~(evaporating temperature (350.degree. C.)~~ of polystyrene ~~is much lower than the crystallization temperature of titania)~~, and second to convert the amorphous titania to crystalline anatase form of titania.

[0032] The result of this procedure is an inverted titania photonic crystal on a substrate such as glass, ITO, FTO coated glass, silicon wafer, quartz, or mica substrate.

[0037] 4) Using negatively charged surfactant stabilized polystyrene spheres with sulfate functional group to make a photonic crystal template on substrate to produce necking between the particles. The necking would benefit the resulting ~~inverse~~ inverted titania photonic crystal film in two ways; it stabilizes the template during infiltration and then during calcination and facilitates removal of the template.

[0038] FIG. 1 shows the ~~absorption~~ UV-Vis spectrum determined at normal incidence to the (111) surface of the ~~macroporous~~ inverted titania ~~inverse opal~~ photonic crystal film.

[0039] FIG. 2 is the scanning electron microscopy image of the cross-section of the ~~macroporous~~ inverted titania ~~inverse opal~~ photonic crystal film on substrate

[0040] FIG. 1 shows the ~~absorption~~ UV-Vis spectrum determined at normal incidence [[of]] to the (111) surface of the ~~macroporous~~ inverted titania ~~inverse opal~~ photonic crystal film produced by following closely the steps in the claim section. The significant sharp ~~transmission dip~~ peak at 425 nm is the ~~pseudo band gap~~ stopgap. ~~resulted from Bragg diffraction from (111) planes of the titania inverse opal structure.~~ The sharpness of the ~~absorption~~ stopgap peak is ~~an indication of strong photonic band gap properties of the film and, in turn,~~ an indication of high quality optical characteristic of the photonic crystal film.

[0041] FIG. 2 is the scanning electron microscopy image of the cross-section of the ~~macroporous~~ inverted titania ~~inverse opal~~ photonic crystal film on substrate. From the highly ordered hexagonal arrangement of the pores from the top layer to the bottom is an indication of the successful uniform infiltration of whole film. The cross-section image is also an indication of successful removal of the polystyrene template from top to the bottom of the film. The high quality and long range order can be seen by drawing a virtual diagonal line on the pores from top to the bottom.

Amendments to the Specification

1. The previous abstract was replaced with a new abstract.

2. In paragraph [0003], the word "[[opals]]" was deleted.

3. In paragraph [0005], the misspelled word "~~waveguids~~" was corrected to "waveguides".

4. In paragraph [0005], the misspelled word "[[die]]" was corrected to "dye".

5. In paragraph [0005], the word "and" was added.

6. In paragraph [0005], the word "~~macroporous~~" was deleted.

7. In paragraph [0005], the word "inverted" was added.

8. In paragraph [0005], the multiword "photonic crystals" was added.

9. In paragraph [0006], the sentences "~~Photonic crystals have the property of filtering white light that is depending on their lattice constant they can forbid the propagation of a particular range of wavelengths from propagation through the~~

~~material, which is reflected instead, and we have a pseudo band gap there. And the remaining wavelengths can pass through the crystal.~~" was deleted.

10. In paragraph [0006], the word "inverted" was added.

11. In paragraph [0006], the multiword "~~inverse opals~~" was deleted.

12. In paragraph [0006], the multiword "photonic crystals" was added.

13. In paragraph [0007], the misspelled word "[[die]]" was corrected to "dye".

14. In paragraph [0008], the word "~~macroporous~~" was deleted.

15. In paragraph [0008], the word "inverted" was added.

16. In paragraph [0008], the word "[[opals]]" was deleted.

17. In paragraph [0008], the multiword "photonic crystals" was added.

18. In paragraph [0008], the "~~fluoride~~" was replaced with "fluorine".

19. In paragraph [0008], "[[and]]" was replaced with "or".

20. In paragraph [0009], the word "~~macroporous~~" was deleted.

21. In paragraph [0009], the word "inverted" was added.

22. In paragraph [0009], the word "[[opals]]" was deleted.

23. In paragraph [0009], the multiword "photonic crystal" was added.

24. In paragraph [0009], the misspelled word "[[power]]" was corrected to "powder".

25. In paragraph [0009], "~~to calcine the alkoxide inside the powder and to remove the polystyrene template it~~" was deleted.

26. In paragraph [0009], the multiword "the powder" was added.

27. In paragraph [0009], the word "~~inverse~~" was deleted.

28. In paragraph [0009], the word "inverted" was added.

29. In paragraph [0009], the word "[[opals]]" was deleted.

30. In paragraph [0009], the multiword "photonic crystal" was added.

31. In paragraph [0010], the word "~~macroporous~~" was deleted.

32. In paragraph [0010], the word "inverted" was added.

33. In paragraph [0010], the multiword "photonic crystal" was added.

34. In paragraph [0011], the word "~~macroporous~~" was deleted.

35. In paragraph [0011], the word "inverted" was added.

36. In paragraph [0011], the word "[[opals]]" was deleted.

37. In paragraph [0011], the word "photonic" was added.

38. In paragraph [0011], the word "crystal" was added.

39. In paragraph [0012], the misspelled word "[[deep]]" was corrected to "dip".

40. In paragraph [0012], the word "~~inverse~~" was deleted.

41. In paragraph [0012], the word "inverted" was added.

42. In paragraph [0012], the word "[[opals]]" was deleted.

43. In paragraph [0012], the multiword "photonic crystal" was added.

44. In paragraph [0012], the sentences "~~The infiltration and densification steps were repeated for 10 times to fill most of the voids inside the silica The titania-silica composite film on substrate produced in the preceding steps was immersed in a warm template~~." were deleted.

45. In paragraph [0013], "The infiltration and densification steps were repeated for 10 times to fill most of the voids inside the silica. The titania-silica composite film on substrate produced in the preceding steps was immersed in a warm " were added.

46. In paragraph [0013], the word "~~inverse~~" was deleted.

47. In paragraph [0013], the word "inverted" was added.

48. In paragraph [0013], the word "[[opals]]" was deleted.

49. In paragraph [0013], the multiword "photonic crystal" was added.

50. In paragraph [0014], the word "~~macroporous~~" was deleted.

51. In paragraph [0014], the word "inverted" was added.

52. In paragraph [0014], the multiword "photonic crystal" was added.

53. In paragraph [0014], the misspelled word "[[deep]]" was corrected to "dip".

54. In paragraph [0014], the misspelled word "[[deep]]" was corrected to "dip".

55. In paragraph [0015], the multiword " ~~a inverse titania opal~~" was deleted.

56. In paragraph [0015], the multiword " an inverted titania photonic crystal" was added.

57. In paragraph [0016], the misspelled word "[[deep]]" was corrected to "dip".

58. In paragraph [0016], the word "~~inverse~~" was deleted.

59. In paragraph [0016], the word "inverted" was added.

60. In paragraph [0016], the multiword "photonic crystal" was added.

61. In paragraph [0016], the multiword "~~a macroporous~~" was deleted.

62. In paragraph [0016], the multiword "an inverted" was added.

63. In paragraph [0016], the multiword " photonic crystal" was added.

64. In paragraph [0018], the word "~~calcinations~~" was replaced with "calcination".

65. In paragraph [0018], the word "[[or]]" was deleted.

66. In paragraph [0018], the words "silicon wafer, quartz, or mica " were added.

67. In paragraph [0019], the multiword "~~(Falcon tube)~~" was deleted.

68. In paragraph [0019], the words "titanium(iv) butoxide, titanium(iv) tert-butoxide, titanium(iv) methoxide, or titanium(iv) propoxide" were added.

69. In paragraph [0019], the words "on a substrate" were added.

70. In paragraph [0019], the word "~~Falcon~~" was deleted and replaced with "centrifuge".

71. In paragraph [0020], the sentence "~~depending on the size of the centrifuge equipment. Basically, the smaller the machine is the faster it should turn to produce same gravitational effect.~~" was deleted.

72. In paragraph [0021], the word "~~Falcon~~" was deleted and replaced with "centrifuge".

73. In paragraph [0022], the word "~~inverse~~" was deleted.

74. In paragraph [0022], the word "inverted" was added.

75. In paragraph [0022], the multiword "photonic crystal" was added.

76. In paragraph [0022], the word "[[band]]" was deleted and replaced with "gap".

77. In paragraph [0022], the word "~~absorption~~" was deleted and replaced with "UV-Vis".

78. In paragraph [0023], the multiword "~~(smaller stop band gap peak)~~"was deleted.

79. In paragraph [0029], the word "and" was added.

80. In paragraph [0031], the word "[[latex]]" was deleted.

81. In paragraph [0031], the word "polystyrene" was added.

82. In paragraph [0031], the multiword "~~(evaporating temperature (350.degree. C.)~~" was deleted.

83. In paragraph [0031], the multiword "~~is much lower than the crystallization temperature of titania)~~" was deleted.

84. In paragraph [0032], the words "silicon wafer, quartz, or mica" were added.

85. In paragraph [0037], the word "~~inverse~~" was deleted.

86. In paragraph [0037], the word "inverted" was added.

87. In paragraph [0037], the multiword "photonic crystal" was added.

88. In paragraph [0037], the word "facilitates" was added.

89. In paragraph [0038], the word "~~absorption~~" was deleted and replaced with "UV-Vis".

90. In paragraph [0038], the multiword "(111) surface of the" was added.

91. In paragraph [0038], the word "~~macroporous~~" was deleted.

92. In paragraph [0038], the word "inverted" was added.

93. In paragraph [0038], the multiword "~~inverse opal~~" was deleted.

94. In paragraph [0038], the multiword "photonic crystal" was added.

95. In paragraph [0039], the word "~~macroporous~~" was deleted.

96. In paragraph [0039], the word "inverted" was added.

97. In paragraph [0039], the multiword "~~inverse opal~~" was deleted.

98. In paragraph [0039], the multiword "photonic crystal" was added.

99. In paragraph [0040], the word "~~absorption~~" was deleted and replaced with "UV-Vis spectrum".

100. In paragraph [0040], the word "[[of]]" was deleted.

101. In paragraph [0040], the multiword "to the (111) surface of" was added.

102. In paragraph [0040], the word "~~macroporous~~" was deleted.

103. In paragraph [0040], the word "inverted" was added.

104. In paragraph [0040], the multiword "~~inverse opal~~" was deleted.

105. In paragraph [0040], the multiword "photonic crystal" was added.

106. In paragraph [0040], the multiword "~~transmission dip~~" was deleted.

107. In paragraph [0040], the word "peak" was added.

108. In paragraph [0040], the multi-word "~~pseudo band gap~~" was replaced with "stopgap".

109. In paragraph [0040], "~~resulted from Bragg diffraction from (111) planes of the titania inverse opal structure~~" was deleted.

110. In paragraph [0040], the word "~~absorption~~" was deleted.

111. In paragraph [0040], the word "stopgap" was added.

112. In paragraph [0040], "~~an indication of strong photonic band gap properties of the film and, in turn,~~" was deleted.

113. In paragraph [0040], the multiword "photonic crystal" was added.

114. In paragraph [0041], the word "~~macroporous~~" was deleted.

115. In paragraph [0041], the word "inverted" was added.

116. In paragraph [0041], the multiword "~~inverse opal~~" was deleted.

117. In paragraph [0041], the multiword "photonic crystal" was added.